CHARACTERIZATION OF POSSIBLE TWO LIQUID LAYERS IN TITAN SEAS. J. Hanley[1,2], J.J. Groven[2,3], W.M. Grundy[1,2], S. Dustrud[2], A.E. Engle[2], G.E. Lindberg[2], S.C. Tegler[2]. [1]Lowell Observatory, Flagstaff, AZ (jhanley@lowell.edu), [2]Northern Arizona University, Flagstaff, AZ, [3]Washington State University, Pullman, WA.

Introduction: Northern Arizona University (NAU) hosts one of a handful of laboratories around the world devoted to studies of astrophysical ices [1, 2]. Many outer solar system bodies are likely to have a combination of methane, ethane and nitrogen. In particular the atmosphere and lakes and seas of Titan are known to consist of these species. Understanding the past and current stability of these lakes requires characterizing the interactions of methane and ethane, along with nitrogen, as both liquids and ices. Previous studies have shown that the freezing point of methane is depressed when mixed with nitrogen [2]. Our cryogenic laboratory setup allows us to explore ices down to 30 K through imaging, and Raman and transmission spectroscopy. Our recent work has shown that although methane and ethane have similar freezing points, when mixed they can remain liquid down to 72 K [3].

The lakes and seas of Titan are composed primarily of methane and ethane, with the concentration of dissolved nitrogen from the atmosphere dependant on the ratio of methane to ethane, the temperature, and pressure. Previous models have predicted the existence of two liquid layers in equilibrium with the vapor phase under certain temperature and pressure conditions [4]. Our previous experiments have confirmed the presence of the two liquid phase at colder temperatures and higher pressures than what exists on the surface of Titan.

Titan's atmosphere is composed of ~1.47 bar of mostly nitrogen. Methane and ethane are quite soluble into each other, and nitrogen is known to be highly soluble into methane, depending on temperature and pressure; however, nitrogen is less soluble into ethane [e.g. 4, 5]. Recent thermodynamic modeling of the ternary liquid of nitrogen-methane-ethane suggest that at higher pressures, such that might exist at depth of a Titan sea, it is possible for a liquid-liquid-vapor equilibrium (LLVE) to occur [4]. Our laboratory work confirmed that LLVE can exist in the conditions predicted by [4]. Here we further explore the possibility that LLVE can exist on Titan, as well as comparing laboratory experiments to the predictions from Cordier et al [4].

Methodology: In the Astrophysical Materials Laboratory at Northern Arizona University, volatile ices are condensed within an enclosed cell (Figure 1). Cooling is provided by closed-cycle helium refrigerators, within vacuum chambers for insulation. Cryogenic ice samples are studied via various analytical techniques including visible and infrared transmission spectroscopy, Raman spectroscopy (Fig 1), and photography (e.g. Fig 2). Mass spectrometers are capable of monitoring changes in composition.

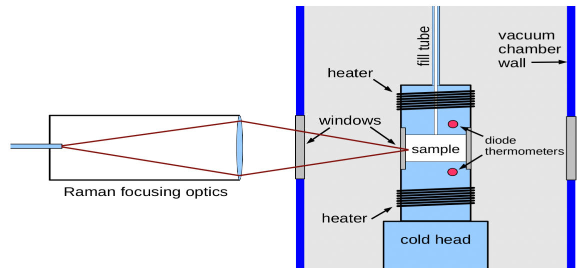

Figure 1. *Schematic of the sample cell and raman optics.*

To test the conditions under which LLVE can form, we first mixed methane and ethane in the gas mixing chamber, condensed them to a liquid in the sample cell at the desired temperature, waiting 20 minutes for equilibrium, then closed the valve between the cell and the mixing chamber. We purged the remaining hydrocarbon gas in the mixing chamber down to vacuum. We slowly opened the valve to allow nitrogen into the sample cell until the desired pressure was reached. Two series of experiments were conducted: (1) testing the predictions in [4], and (2) testing how close to Titan surface conditions the LLVE would occur. Along the way we also varied the initial hydrocarbon ratio to see how that affected LLVE formation and composition. In all experiments, once the desired T and P conditions were met, we agitated the sample to ensure full mixing, waited 20 minutes for equilibrium, agitated again, then visually inspected the sample, taking photographs and videos. If the liquid was homogeneous, we would take one Raman spectrum in the middle of the liquid to determine composition. If any stratification was present, including density lines or LLVE, then Raman spectra would be taken in 1 mm increments from the bottom of the cell to 1 mm above the liquid to ensure the gas phase was also sampled.

Results: In all experiments performed so far, the lower layer is enriched in nitrogen and methane, while the upper layer is enriched in methane and ethane, although both layers have all three species present. The initial ratio of methane to ethane will control the relative volumes of the two liquids, though it does not appear to affect their compositions. Comparing to Cordier et al. [4], we find the two liquid phase does not form at 85 K until a pressure of greater than ~1.83 bar is reached, compared to the 1.7 bar predicted. Our results show that at Titan surface pressure (1.47 bar), a mixture of methane, ethane and nitrogen will remain in one liquid down to 82 K, where it will then split into two liquids. We will present these experimental results detailing the conditions under which the two liquid phases form, as well as the composition of the liquids. These results can inform whether they might occur on Titan, and how that might impact understanding of previous mission results from Cassini, as well as future missions, and guide current theoretical models.

Modeling: We have undertaken computational molecular dynamics simulations to examine the molecular origins of the behavior we have observed. Simulations of the pure species reveal densities that deviate from experiment by 8%, 1%, and 27% for methane, ethane, and nitrogen at 100 K. Simulations of methane, ethane, and nitrogen mixtures have then been used to predict properties of both the upper and lower liquid layers. For example, estimated compositions of each layer provide densities that justify layer order, which are found to be in general agreement with predictions by Cordier et al [4].

Implications: Our experiments show that within the depths measured in the seas and temperatures and pressures expected there, two liquid layers are possible on Titan today. Some interesting questions that are raised are what happens when considering the circulation patterns of the largest seas, how the "pure" methane rain (saturated with nitrogen) or the rivers would affect the delicate equilibrium necessary for LLVE to occur. Additionally, this calls into question what types of ice would be likely to form in each layer, depending on their position within the lake, temperature, pressure, and composition (see Engle et al, this conference [6], for more discussion of ethane ice formation).

Future Work: We next plan to undertake simulations of the two liquid layers in contact with each other. This will permit characterization of molecular behavior in the whole system, including interfacial organization of the molecules, molecular flux across the boundary, and other characterization of the two-phase equilibrium.

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References: [1] Hanley J. et al (2016) *LPSC* Abstract #2421. [2] Protopapa S. et al (2015) *Icarus 253*, 179–188. [3] Hanley J. et al (2017) *LPSC* Abstract #1686. [4] Cordier D. et al (2017) *Nat. Astro. 1*, 0102. [5] Malaska M.J. et al (2017) Icarus *289*, 94–105. [6] Engle, A.E. et al (2019) *LPSC* Abstract #2509.

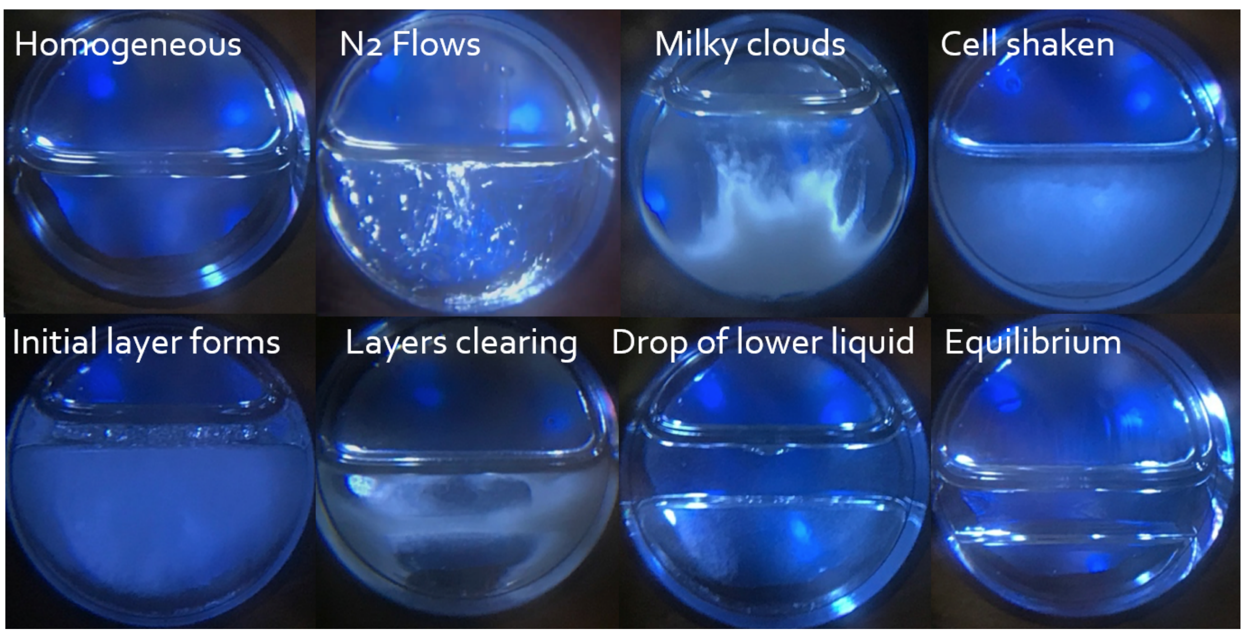

Figure 2. *Images taken of two-layer system formation. Note: Not all images are from same experiment. a.) The clear homogenous sample. b.) Nitrogen flows into the liquid. c.) Sudden flush of milky material sinks to bottom. d.) After agitating cell to mix milky liquid. e.) Interface beginning to form after agitation. f.) Cloudiness gradually decreases revealing more of interface. g.) A drop of nitrogen-rich liquid falling from meniscus. h.) The system in equilibrium.*